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Qualification of the ALKASORB sorbent for the sorption-enhanced water-gas shift process

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Abstract

For the sorption-enhanced water-gas shift (SEWGS) process, a new sorbent material has been qualified in a reactor of 2 m length under conditions close to industrial designs. The sorbent ALKASORB is a potassium-carbonate promoted hydrotalcite-based compound. ALKASORB is shown to have many favourable properties in comparison to the reference sorbent, in particular with respect to mechanical stability. The cyclic capacity of the new compound is substantially higher than the cyclic capacity of the reference sorbent, and it allows a reduction of the steam requirement of 50%. The sorbent has demonstrated catalytic activity for the water-gas shift reaction that is sufficient to omit a separate catalyst. It is demonstrated that the sorbent remains chemically and mechanically stable during operation of at least 2000 adsorption – desorption cycles, even in the presence of H_2S in the feed. H_2S is shown not to influence CO_2 adsorption capacity and is co-captured with the CO_2. In contrast to the reference material that showed mechanical degradation during extended adsorption – desorption cycles, the new material is stable and allows to obtain carbon capture levels exceeding 95% more efficiently and more economically since the required size of the vessels will be smaller.

Keywords: sorption-enhanced reaction; carbon capture; high temperature sorbent; pressure swing; hydrotalcite; hydrogen sulphide

1. Introduction

Pre-combustion carbon capture technologies are potentially well suited for decarbonising gas turbine fuels, in particular if warm gas separations can be achieved. The sorption-enhanced water-gas shift (SEWGS) process is an advanced pre-combustion carbon capture technology that can yield high capture ratios at lower efficiency penalties and at lower costs than commercially available solvent scrubbing technologies. SEWGS is a pressure swing adsorption (PSA) process based on reversible CO_2 adsorption on solid materials at temperatures between 350 and 550 °C. Accordingly, substantial efficiency improvements are achieved since cooling and partially condensing the fuel gas and subsequent reheating

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upstream of the gas turbine are avoided. The reactor vessels contain a packed bed of sorbent pellets, optionally mixed with water-gas shift catalyst pellets. As CO_2 is removed from the synthesis gas by adsorption, CO is simultaneously converted to CO_2 by the water-gas shift reaction, which increases the carbon capture ratio further. The sorbent is periodically regenerated by purging with steam at low pressure.

At the GHGT-10, it was shown that a new sorbent could solve two issues of the sorbent tested previously: the loss of mechanical and chemical stability (gradually increasing slip of CO_2 over time) under realistic operating conditions [1]. The new sorbent, denoted as ALKASORB, is a magnesium and aluminium containing hydrotalcite, which was promoted with potassium carbonate [2]. Additional advantages of ALKASORB are the higher density and the higher crush strength. The ALKASORB compound is now qualified under realistic process conditions.

2. Method

Measurements of CO_2 adsorption isotherms under realistic industrial conditions using a mass suspension balance remains a challenge due to the presence of high pressure steam and the coadsorption of steam. Hence, isotherms were approximated using breakthrough measurements in a packed bed reactor. Figure 1 shows a flow scheme of the rig with a 2 m long reactor vessel, which was packed with ALKASORB pellets calcined at 400 °C. Feed gases were heated to 400 °C in electric heaters and the reactor walls were kept at 400 °C by electric heating and insulation. Product gases were cooled down to 5 °C and condensate was removed in knock-out drums. Gas quantities of dry product gases were measured by volumetric dry gas meters. Feed gas pressure was 28 bar, and N_2 was balance component. Breakthrough capacities were calculated using the velocity of the thermal wave resulting from the sorption process and corrected for the CO_2 contained in the reactor gas voids. Gas compositions were measured with non-dispersive infrared equipment. For H_2S measurements, a mass spectrometer was used, samples were taken directly from the product end of the reactor. Sour gas samples were cooled thereby condensing steam, then expanded to atmospheric pressure, dried, and diluted with Ar. The continuous process was demonstrated in a test rig using five parallel reactors, each of 6 m length. Water-gas shift activity was measured in a parallel flow rig by increasing temperature in 10 °C steps from 300 to 500 °C and back. Samples of 100 mg were used, GHSV was 60,000 $l \cdot g^{-1} \cdot h^{-1}$, feed composition was 13.3% CO, 6.7% H_2, 26.7% H_2O, 53.3% N_2. Thermodynamic calculations were performed in Factsage v5.5.

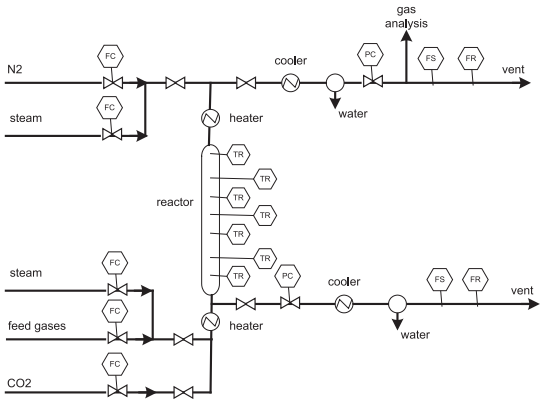

Figure 1 Flow scheme of the test rig.

3. Capacity

CO_2 adsorption isotherms are approximated by measuring breakthrough capacities over a range of CO_2 partial pressures at 400 °C for the ALKASORB and reference sorbents using a dry feed gas at a 10 slpm flow rate. The observed capacities are fitted to Langmuir isotherms $q_{CO2}^* = m \cdot b \cdot P_{CO2} / (1+b \cdot P_{CO2})$, where q_{CO2}^* (mołkg $^{-1}$) is the average equilibrium solid-phase concentration, P (bar) the pressure, and m (mol·kg^{-1}) and b (bar^{-1}) model constants. The results presented in Figure 2 show that ALKASORB has a substantially higher capacity than the reference sorbent. The formation of $MgCO_3$ in the reference sorbent, leading to additional CO_2 uptake [3], is expected to be negligible due to the absence of steam. The loading of hydrotalcite-like compounds with CO_2 at 400 °C is reportedly a combination of primarily physisorption and secondly chemisorption [4], which is in agreement with the observed relatively high loadings at the lowest partial pressures. For these compounds, a Langmuir single-component adsorption isotherm would therefore be a first approximation. For ALKASORB, b is 4.45 bar^{-1} and for the reference sorbent b is 0.46 bar^{-1}.

Furthermore, adsorption isotherms in the absence and in the presence of 20% steam are measured and compared, indicating that adsorption capacities are about 10% lower if steam is present in the feed (Figure 3). By comparison, Mayorga et al. [5] reported that at 10 bar steam conditions, capacities are similar under dry and wet conditions. Other studies [6 – 9] report slightly higher capacities under wet conditions, but these were all measured at low steam partial pressures. At 400 °C, the sorbents are completely dehydrated and partially dehydroxylated. Steam present in the feed gas may maintain the hydroxyl concentration of the surface. The magnesium and aluminium hydroxides are believed to activate adsorption sites [7] and form bicarbonates [6] or carbonates [10] in the presence of CO_2. The differences observed in the effect of steam can be attributed to the different initial conditions of the sorbent. Capacities are known to be dependent on the regeneration conditions used prior to the adsorption experiment [10]. Before adsorption experiments, ALKASORB was always completely regenerated with steam, whereas in the other studies the sorbent was regenerated with dry gases. In the latter case, steam in the feed may rehydroxylate the sorbent, which increases CO_2 adsorption, and in the former case steam may enhance sorbent regeneration, and thus decrease the reversible CO_2 physisorption. For process simulations, the adsorption isotherm measured in the presence of steam should be used since the SEWGS feed gases contain typically 10 – 30% steam.

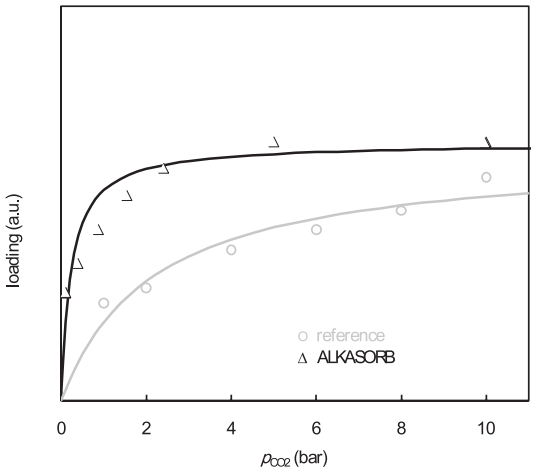

Figure 2 Single component adsorption isotherms for ALKASORB and reference material, dry conditions, 400 °C

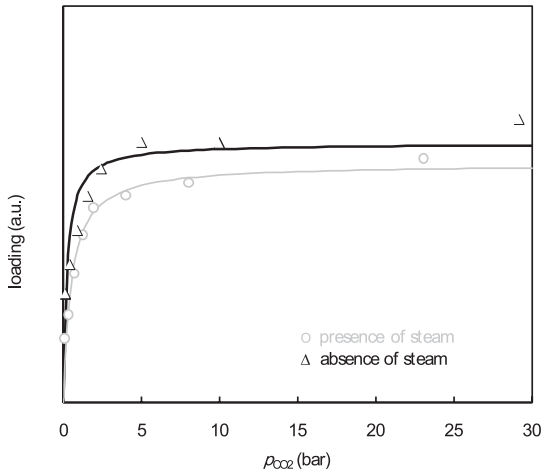

Figure 3 Adsorption isotherms for ALKASORB, in the absence and presence of steam in the feed (400 °C)

In separate experiments the regenerated and subsequently dried sorbent was contacted with steam, and from the temperature rises in the column and speed of the thermal wavefront it was concluded that a substantial amount of steam is taken up, which is attributed to rehydration and partial rehydroxylation of the sorbent. The amount of steam retention with the hydrotalcite-based compounds are similar to the amounts reported in literature [6, 7].

4. Chemical activity and stability

There are three strong drivers for integrating the water-gas shift catalytic activity in the sorbent compound. Omitting the catalyst will bring substantial CAPEX and OPEX savings through reduction of the vessel volumes. It will also increase H_2 recovery and improve the purity of the CO_2 stream due to the absence of a redox reaction on the catalyst, taking place in the presence of steam during the regeneration step. In applications where the syngas contains substantial amounts of H_2S, such as in coal gasification plants, a sour shift catalyst would be required, since a sweet shift catalyst would be rapidly poisoned by H_2S in the feed gas. Nonetheless, thermodynamic calculations show that the sour shift catalyst may deactivate at the hydrogen product end of the bed within a few hundred cycles due to desulphiding during the rinse and purge steps of a typical SEWGS cycle. Hence, sufficient catalytic activity of the sorbent is essential for sour applications.

The catalytic activity for the water-gas shift reaction is measured for both the ALKASORB and the reference sorbent in a parallel flow apparatus in the range from 300 to 500 °C at atmospheric pressure, showing a markedly improved activity for ALKASORB over the reference sorbent (Figure 4).

Small scale tests had indicated that the water-gas shift activity of ALKASORB may even be sufficient to omit the separate water-gas shift catalyst in a SEWGS reactor if the syngas contains 200 ppm H_2S [11]. This is confirmed by performing breakthrough tests at 28 bar in the 2 m reactor packed with sorbent in the absence of a catalyst, feeding a mixture of 15% CO_2, 8% CO, 52% H_2 and 25% H_2O, without H_2S. As

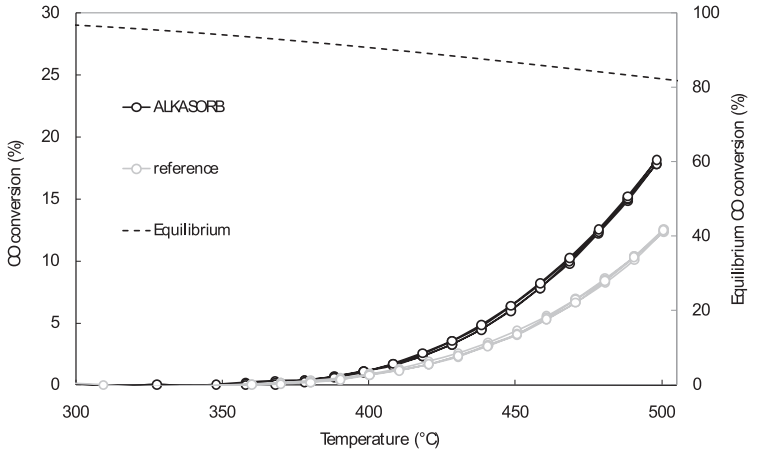

Figure 4 Water-gas shift activity for ALKASORB and reference sorbent

shown in Figure 5, full CO conversion is obtained until CO_2 and CO start to break through simultaneously, which is key for the SEWGS process. After breakthrough the conversion is 44%, which is substantially below thermodynamic equilibrium. Reconciliation of the hydrogen and carbon balances confirms the presence of the shift reaction. This experiment shows that a separate catalyst is not required for the SEWGS process. Even if the temperature is reduced from 400 to 300 °C, activity well before CO_2 breakthrough is sufficient to obtain full CO conversion, although the breakthrough for CO starts slightly earlier than for CO_2, and after breakthrough conversion is limited (Figure 6). The peak CO level well above the feed concentration is higher than a mere concentration effect would cause, indicating that CO might desorb from adsorptive sites, which are required for catalytic activity. From the breakthrough time of CO and CO_2 at 300 °C and 400 °C, it can be calculated that the breakthrough capacity is 25% higher at 300 °C than at 400 °C. By comparison, Mayorga et al reported a 50% higher capacity at 300 °C, for a sorbent similar to the reference sorbent [5].

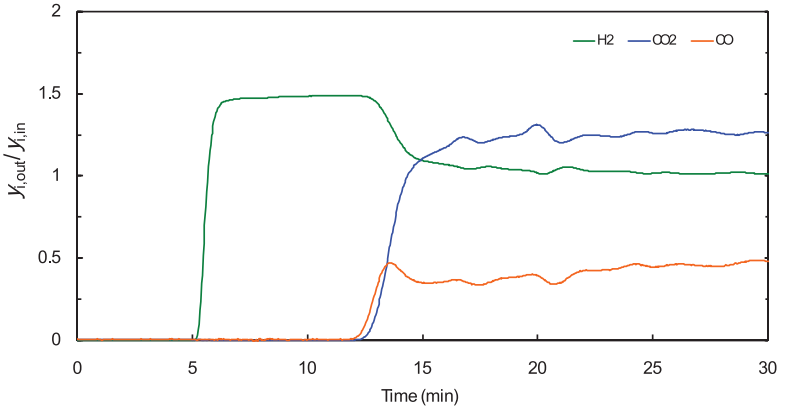

Figure 5 Breakthrough tests showing full CO conversion before breakthrough in the absence of a catalyst (400 °C)

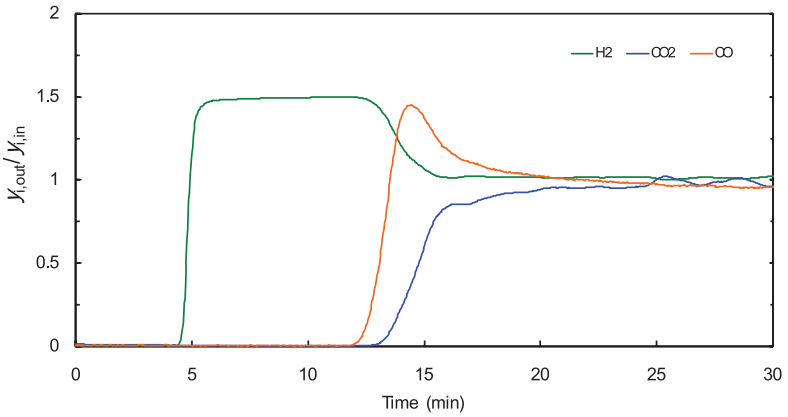

Figure 6 Breakthrough tests showing full CO conversion before breakthrough in the absence of a catalyst (300 °C)

The stability of the sorbent is investigated under cyclic conditions. A cycle consisted of five consecutive steps: (1) feed, during which adsorption and shift reaction occurred; (2) countercurrent rinse with high-pressure steam, for removing the gas present in the voids; (3) countercurrent depressurization; (4) countercurrent purge with low-pressure steam, for regeneration of the sorbent at atmospheric pressure; and (5) countercurrent repressurisation with N_2 and steam. The feed gas contained 15% CO_2, 9% CO, 52% H_2, 24% H_2O. In Figure 7, the dots show the dry CO_2 and CO fractions in the product gas at the end of the feed step for each cycle number, and the line is the moving average over 10 cycles. During the measurement period the carbon slip is so low that carbon recoveries of 99% are obtained. The CO and CO_2 concentrations at the end of the feed step are extremely sensitive to small changes in process conditions and drift in the gas analysis, because both gases start to break through at that moment. Therefore, the slow trend towards slightly higher CO levels is within the margin of experimental error. The mixing cup averaged CO concentrations are lower than the CO concentrations at the end of the feed step. Mixing cup averages were 0.04% for cycles 45 – 55 and 0.09% for cycles 1970 – 1980. Thus, the CO conversion can be calculated to start at 99.6%, decreasing slightly to 98.9% after cycle 1300. This small decrease of conversion can be linked to the small decrease of the CO_2 capture rate, which shifts the chemical equilibrium towards slightly higher CO_2 and CO slip; it does not indicate a deactivation of the catalytic properties of the sorbent for the WGS reaction. Apparently, the sorbent is chemically stable over at least 2000 adsorption – desorption cycles. After the test, the amount of CO_2 recovered during the full regeneration was recorded; the amount was equal to the breakthrough capacity within 10%, which indicates the absence of formation of $MgCO_3$ during the duration test. Unloading of the reactor revealed that the sorbent pellets are mechanically stable as well.

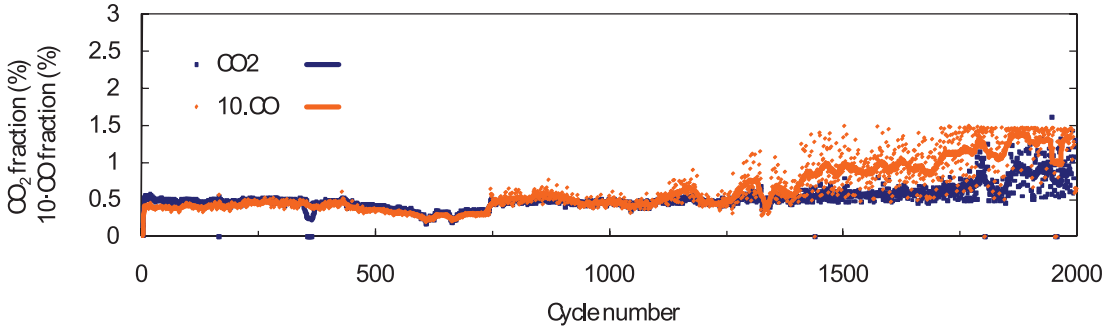

Figure 7 A stable product gas composition over 2000 cycles

5. Sulphur removal

The cocapture of H_2S and CO_2 by ALKASORB in the presence of H_2, CO and H_2O is confirmed by completing breakthrough tests in the 2 m tall reactor in the presence and absence of H_2S. The feed contained 46% H_2, 13% CO_2, 8% CO, 22% H_2O, balance N_2, and in the second breakthrough test H_2S in He was added to attain a 200 ppm H_2S level. Figure 8 shows that CO_2 breaks through at exactly the same time in both cases, confirming that H_2S does not influence the CO_2 adsorption capacity. Also the slope of both CO_2 breakthrough curves are identical within the experimental error. These results are in agreement with the observations by Van Dijk et al [11], who performed tests on smaller scale and with a different cycle and a different feed composition. H_2S and CO_2 break through simultaneously, and H_2S and CO_2 are cocaptured. The oscillations after breakthrough are caused by an unstable pressure regulation.

A long-term test was performed with the same cycle as for the test shown in Figure 7, and a feed gas containing 15% CO_2, 8% CO, 24% H_2O, 10% H_2, balance N_2, at a pressure of 29 bar. The level of H_2S in the feed gas, initially 50 ppm, was increased to 100 ppm after cycle 250 and to 200 ppm after cycle 500. Figure 9 shows the slip of CO_2, CO, and H_2S in the sampled top product gas over time. During the test

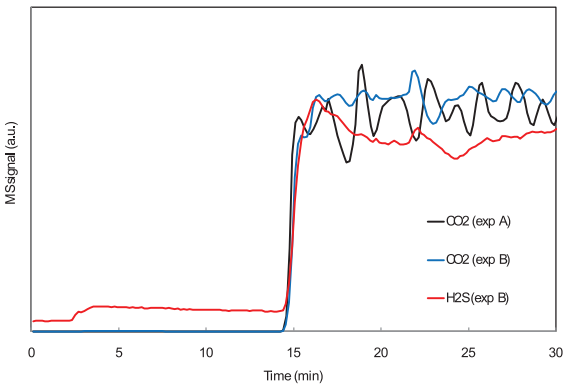

Figure 8 Breakthrough of CO_2 in the (A) absence and (B) presence of H_2S (400 °C)

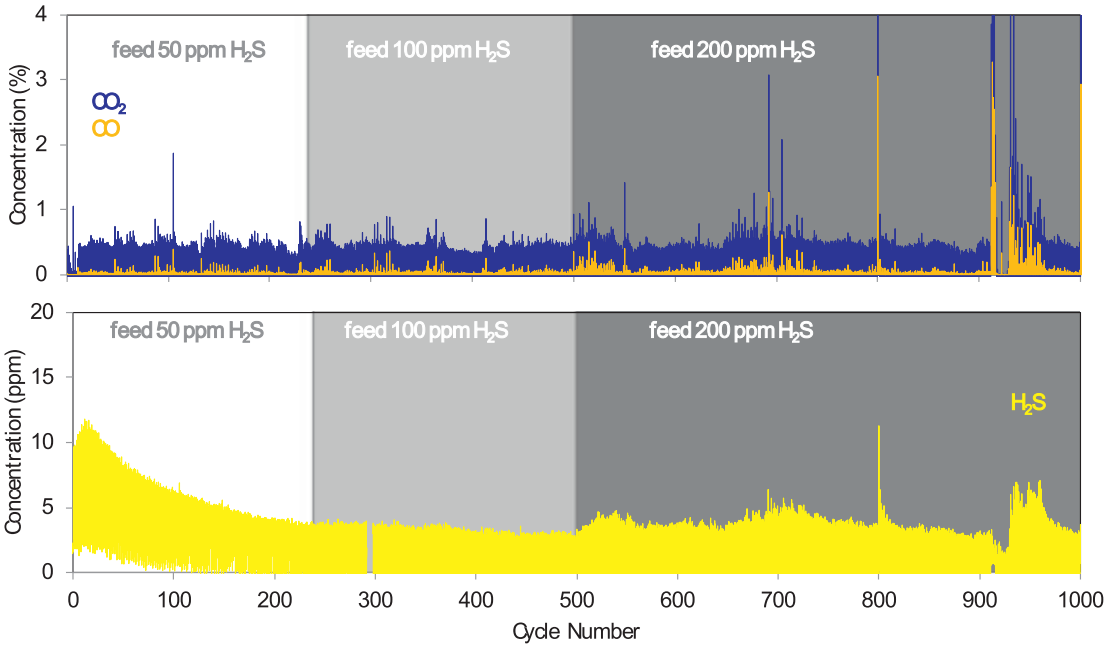

Figure 9 Stable removal of (upper) CO_2 and CO and (lower) H_2S

steam feed was interrupted during cycles 910 – 930, and in that period the CO feed was switched off as a precaution. After the upset, slip levels approximate their steady levels. The test confirms that the sorbent is stable over 1000 cycles in the presence of 200 ppm H_2S in the feed gas. In total over 8000 cycles have been achieved with one batch of ALKASORB.

6. Demonstration of a full cycle using the multi-column test rig

Further qualification of ALKASORB is obtained by continuous operation in a test rig with five reactors. The feed pressure was 25 bar, and the feed gas consisted of 17% CO_2, 24% H_2O, balance N_2. These tests show that a total steam-to-carbon ratio below 2.0 mole/mole is feasible, which is required to be advantaged over wet scrubbing technologies in power plants with carbon capture. Thus, ALKASORB allows steam consumption to be reduced by more than 50% compared to the reference material [12]. Moreover, it was observed that the effect of operating temperature is limited in the range between 390 and 420 °C, as Figure 10 shows that cyclic capacities vary within 1% in that temperature range. Equilibrium loading is fairly insensitive to temperature in the investigated temperature range [9], and the slightly higher cyclic capacities observed for higher temperatures are attributed to the increased desorption rate. Further tests without N_2 in the feed demonstrate that by reducing the feed flow rate, a product gas containing 99.99% H_2 may be obtained.

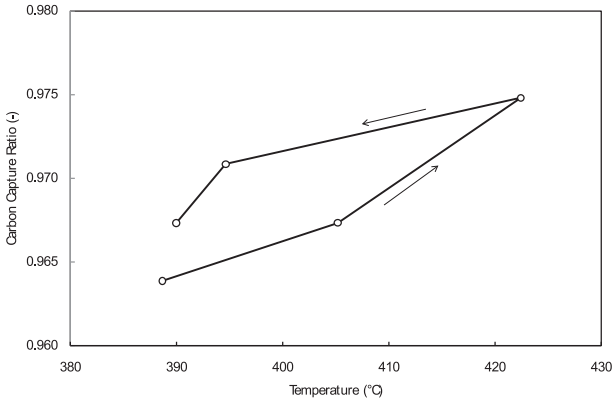

Figure 10 Effect of temperature on carbon capture ratio

Table 1 provides an excerpt of results, indicating that cyclic capacity and top product purity cannot be maximized simultaneously. The high purity is obtained by increasing the length of the unused bed and increasing the purge flow rate. High gas purities are important for gas purification applications of SEWGS such as H_2 production, whereas maximizing cyclic capacities is more important for CCS applications.

7. Conclusions

The ALKASORB sorbent has been qualified in two process development units at 2 – 25 kg sorbent scale. The cyclic capacity of the compound is higher than the cyclic capacity of the reference sorbent, and steam requirement is reduced by more than 50%. The sorbent remains mechanically and chemically stable during operation of at least 2000 adsorption – desorption cycles. The sorbent has sufficient catalytic activity for the water-gas shift reaction so that a separate catalyst can be omitted. With this new compound, carbon capture levels exceeding 95% can be obtained more efficiently, vessels will be smaller, and SEWGS is expected to be competitive with conventional CO_2 removal technologies in NGCC and IGCC power plants [13, 14]. ALKASORB has now been qualified sufficiently to move on to the next level of development, which is the scale-up to a pilot unit planned for the near future. The pilot unit would operate on a slip stream of an industrial gas and would be designed to capture 35 ton CO_2 per day.

Table 1 Performance under varying operating conditions

CO_2 feed flow	Steam-to-carbon ratio during purge	Top product purity	Carbon capture ratio	Relative cyclic Capacity
Nltr/min	mole/mole	%	%	-
7.3	1.1	98.7	96.4	1.00
6.3	1.3	99.63	98.8	0.89
5.4	2.2	99.99	99.98	0.85

Acknowledgement

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